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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Hydrogenolysis Process

We, HALCON INTERNATIONAL, INC., of 2 Park Avenue, New York, 16, New York, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

THIS INVENTION relates to the production of aralkanes from the corresponding aralkyl alcohols.

The use of alpha-aralkyl hydroperoxides in the epoxidation of olefins has distinct advantages over other epoxidation methods suggested by the prior art such as oxidation with a peracid or with an oxygen-bearing gas. High yields, fast reaction rates, low cost and safe operating procedures are important features of this method of epoxidation.

A by-product of the epoxidation reaction is the alpha-aralkyl alcohol which may have no substantial commercial use and which, if unreclaimed, represents a major economic burden to the process. By the term 'alpha-aralkyl alcohol' we mean a compound in which an aromatic group and a hydroxy group are attached to the same carbon atom of an alkyl group.

One method of reclaiming the alcohol is to convert it to the corresponding aralkane and this may be achieved by subjecting it to hydrogenolysis in the vapour phase in the presence of a catalyst to form the aralkane. This process requires a reaction at elevated temperatures and equipment to carry out the reaction in the gas phase.

It is an object of this invention to provide an improved process for the hydrogenolysis of alpha-aralkyl alcohols to the corresponding aralkanes.

In accordance with the present invention alpha-aralkyl alcohols are subjected to hydrogenolysis in the liquid phase in the presence of a platinum group metal catalyst and at a temperature of above 50°C, preferably above 80°C, but not above 120°C, whereby high yields to aralkanes are obtained.

A totally unexpected catalytic phenomenon has been discovered. It is common in the art that catalysts tend to deactivate more rapidly at higher temperatures and tend to retain their activity longer at lower temperatures. In this system the inverse is true. When operating at temperatures below 80°C., catalyst activity decreases; after a period of hours, the rate of conversion of alcohol is much lower than at the start of operation. However, if the catalyst is regenerated by solvent washing it is possible to achieve high rates of conversion, although a catalyst deactivation again will occur and the rate of conversion will eventually reach the same level as before catalyst regeneration. At temperatures above 50°C. the deactivation phenomenon is less marked and at temperatures above 80°C. negligible deactivation occurs.

This deactivation phenomenon is attributed to an adsorption of some material formed as an intermediate in the reaction sequence, on the active catalyst sites. It is not thought to be due to an impurity in the feed alcohols since even the most highly purified alcohols exhibit the same effect. Almost any inert solvent either aqueous or non-aqueous can be used in the solvent-wash regeneration, but those most preferred are those indigenous to the system such as the pure alcohol or the pure alkylaromatic compound. The regeneration may be carried out by thoroughly contacting the catalyst with solvent for a period

of from 5 minutes to 10 hours; usually one hour suffices for complete regeneration. The regeneration is carried out more quickly and effectively if high volumes of solvent are used, if the catalyst is agitated in the solvent and if high solvent temperatures are employed. Suitable solvents are cyclic or acyclic hydrocarbons, oxygenated compounds such as water, ethers, alcohols, esters, acids and ketones. Specific examples of preferred solvents are cumene, ethylbenzene, alpha-phenylethanol, dimethylphenylcarbinol, benzene and toluene.

Reaction temperature has an effect on the hydrogenolysis other than with respect to catalyst activity. In general, conversion of alcohol is increased with operation at higher temperatures, but at temperatures above 120°C. hydrogenation of the aromatic ring takes place with consequent loss in yield.

The catalyst which is used in the conversion of alpha-alkylaromatic alcohols in the process of the invention is chosen from among the platinum group metals and their compounds. Suitable catalysts are the elementary form or compounds of platinum, iridium, osmium, palladium, and rhodium. A preferred catalyst is palladium.

The catalyst may be in such combined forms as oxide, halide, sulphide, sulphate and phosphate, or as a double salt. Specific examples of such catalysts are palladium chloride, platinum chloride, palladium oxide, platinum oxide, palladium sulphate, palladium phosphate, palladium sulphide, and the corresponding compounds of the other platinum group metals.

The catalyst may be supported on a broad range of inert supports such as silica gel, magnesium carbonate, alumina, kieselguhr, carbon, barium sulphate and asbestos. These supports may be in granular or pelleted form having a large surface to volume ratio. Carbon and aluminas have been found to be particularly satisfactory supports.

The percentage of the catalytic material on the support may be generally from 0.05 to 50% by weight of the support, but desirably is between 0.1% and 20%.

The liquid feed may be pumped through the catalyst bed or tricked through it or otherwise contacted with it to ensure good liquid-catalyst interaction. The space velocity defined as volume of liquid feed per volume of catalyst and support may be in the range of 0.01 to 100 reciprocal hours. In general the conversion of alcohol is increased as the space velocity is decreased.

Unconverted alcohol is separated from the aralkane compound by distillation; the alcohol is the bottoms product. Small amounts of phenol which may be present in the system and has acidic properties may tend to degrade the alcohol during distillation and

cause a loss in yield. For this reason it is desirable that all the alcohol be converted during hydrogenolysis.

The liquid feed to the hydrogenolysis can be the effluent of an epoxidation reaction in which an olefinically unsaturated compound has been epoxidised by means of an alpha aralkyl hydroperoxide which has itself been converted to an alpha aralkyl alcohol. Epoxidation reactions of this type are described in our earlier applications 50666/63 (Serial No. 1074330) and 87/65 (Serial No. 1097132), among others. From the effluent epoxides, unconverted olefins and light ends are removed and the residue is freed, usually by a simple flash technique, of heavy residues and catalyst from the epoxidation step prior to use in the hydrogenolysis process of the invention. The resulting feedstock will contain traces of unconverted alpha-aralkyl hydroperoxide, phenol and by-product aralkyl ketone as well as the alpha-aralkyl alcohol. Additionally, aralkane from which the hydroperoxide was formed and solvent used in the epoxidation reaction may be present. Typical feed mixtures will contain generally from 10 to 80% alcohol, 20 to 80% aralkane, less than 1% ketone and less than 1% phenol. However, it is possible to operate outside these ranges as well.

In the preferred method of operation, the epoxidation effluent is stripped of unconverted olefin, epoxide and other light ends and then flashed at 130°C. and 100 mm Hg; residue, epoxidation catalyst and some alcohol are removed as a bottoms product and recycled to the epoxidation step. The flashed vapour is condensed and subjected to hydrogenolysis.

Hydrogen, fed as pure gas or in conjunction with other inert gases, may be introduced to the catalyst-liquid system either co-currently or counter-currently. It may be provided in excess of the stoichiometric requirement or in quantities less than the stoichiometric requirement; however, since complete alcohol conversion is desirable it is preferably supplied in excess.

Hydrogen partial pressure has a marked effect on alcohol conversion. Conversion is increased as hydrogen partial pressure is increased. Desirably, the pressure should be 20 to 1000 p.s.i.g., and preferably 50 to 200 p.s.i.g.

The effluent from the hydrogenolysis is further processed by one of two schemes. The first scheme is comprised of an initial distillation to remove small amounts of light ends that have formed, followed by a distillation to remove phenol as a bottoms product. The aralkane may then be converted to an alpha-aralkyl hydroperoxide which may be recycled to the epoxidation step.

The second scheme includes a water extraction of the hydrogenolysis effluent to remove

phenol and a light-ends distillation to purify the aralkane prior to recycle.

The present invention is applicable to epoxidations in which there is used as the organic hydroperoxide a hydroperoxide having the formula ROOH where R is a substituted or unsubstituted alpha aralkyl radical, preferably having 8 to 20 carbon atoms. The preferred hydroperoxides are cumene hydroperoxide, ethylbenzene hydroperoxide, p-ethyl toluene hydroperoxide, and diisopropylbenzene hydroperoxide. Cumene hydroperoxide is an especially effective compound.

The catalysts which are most effective in the epoxidation reaction include compounds of the following metals: Ti, V, Cr, Cb, Se, Zr, Nb, Mo, Te, Ta, W, Re, U. These metals may be characterized as forming peracids or as hydroxylation catalysts. By far, the preferred catalysts are V, Ta, Ti, Mo, W, Nb, Te, Re, or Se catalysts. Mixtures of catalysts may also be used.

These compounds may be added in a form initially soluble in the reaction medium. While solubility will of course depend on the particular reaction medium a suitably soluble substance would be a hydrocarbon soluble, organic compound of one of the above-mentioned metals having a solubility in methanol at room temperature of at least 0.1 gram per litre. Illustrative soluble forms of the catalytic compounds are the naphthenates, stearates and carbonyls. Various chelates, association compounds and enol salts, such as aceto-acetonates may also be used. The most preferred catalysts are compounds of vanadium and molybdenum such as naphthenates and carbonyls.

The amount of catalyst employed in the epoxidation is suitably at least 0.01 millimoles of metal per mole of peroxy compounds. Preferably from 0.02 to 40 millimoles, and desirably 0.1 to 4.0 should be used.

The olefinic materials which can be epoxidized include both substituted and unsubstituted olefinic and alicyclic olefins which may be, for example, hydrocarbons, esters, alcohols, ketones or ethers having from 2 to 20 carbon atoms, and preferably at least 3 carbon atoms. Illustrative olefins are ethylene, propylene, normal butylene, isobutylene, the pentenes, methyl kentenenes, octenes, dodecenes, cyclohexenes, and methyl cyclohexenes. Halogen, oxygen or sulphur substituted olefins can also be used. These are illustrated by allyl alcohol, allyl mercaptan, cyclohexanol, methylmethacrylate, methyl oleate and allyl chloride.

Temperatures required for epoxidation are broadly in the range of -20 to 200°C . and preferably 60 to 120°C . Pressure conditions, illustratively atmospheric to 1000 p.s.i.g., must be sufficient to maintain the liquid phase.

The epoxidation reaction time may be from 1 minute to 10 hours depending upon the activity of the materials employed and the desired conversion. Normally, reaction times from about five minutes to 4 hours are employed.

The ratio of olefinically unsaturated compound to organic hydroperoxide in the epoxidation step is broadly in the range of 1:15 to 20:1 and preferably 2:1 to 5:1. The initial hydroperoxide concentration will normally be 1% or more although lesser concentrations are also effective.

It is generally desirable that the epoxidation reaction be carried out in the presence of a solvent. Suitable substances are olefinic, naphthenic, or aromatic hydrocarbons and their oxygenated derivatives. Alcohols, ketones, ethers and esters are particularly advantageous and the presence of alcoholic or ketonic substances has frequently been useful even when the major solvent is a hydrocarbon material. Preferred solvents are those which have the same carbon ring structure as the hydroperoxide being used. Solvent loss and separation problems are minimized in this fashion.

The following examples illustrate the invention, Example III and the corresponding parts of Examples IV to IX being included for comparative purposes only. Unless otherwise indicated all percentages and parts are on a weight basis.

EXAMPLE I

A mixture consisting of 13.5 parts of cumene hydroperoxide, 23.0 parts of cumene, 35.0 parts of dimethylphenylcarbinol, 0.4 parts of Mo naphthenate (containing 5% Mo), 0.1 parts of Na naphthenate, and 28.0 parts of propylene was pumped through a reaction chamber held at a temperature of 110°C . and a pressure of 650 p.s.i.g. Residence time of the reaction mixture in the reactor was about 2 hours.

The reaction mixture was then distilled to remove unreacted propylene and propylene oxide product; the undistilled bottoms consisted of 23.0 parts of cumene, 47.1 parts of dimethylphenylcarbinol, 0.4 parts of Mo naphthenate, and 0.1 parts of Na naphthenate. This mixture was then flashed at 130°C . and 100 mm Hg. The liquid phase containing essentially all of the Mo naphthenate and Na naphthenate catalyst and a small amount of dimethylphenylcarbinol was recycled to the epoxidation step. The vapour phase was condensed and further treated as set forth below.

A hydrogenolysis reactor consisting of a $1/2$ " diameter steel tube was loaded with 16 grams of catalyst prepared as follows:

95 grams of 12/40 mesh activated granular carbon was added to a PdCl_2 solution prepared by dissolving 8.4 grams Pd Cl_2 in 160

cc. of 6 N HCl. The mixture was boiled gently for 1 hour and then allowed to stand overnight. The mixture was then placed in a rotary catalyst dryer and heated to evaporate the water. The dry catalyst particles were then transferred to a glass tube contained in a furnace. The tube was flushed with nitrogen, the temperature raised to 90° C., and hydrogen flow introduced. The temperature was raised slowly to 100° C. and was then maintained at 110° C. for 1 hour. The temperature was then raised to 200° C. at the rate of 25° C./hr. and held at 200° C. overnight with the flow continuing. When the effluent hydrogen showed no further traces of chloride, the catalyst was flushed with nitrogen and cooled.

The alcohol-cumene mixture was fed to the hydrogenolysis reactor at a space velocity of 0.5 hr⁻¹, hydrogen being introduced to maintain a partial hydrogen pressure of 200 p.s.i.g., and the temperature being maintained at 80° C.

After 4 hours of operation, the conversion of alcohol to cumene was 99%, and after 24 hours of operation, the conversion was 99%.

EXAMPLE II

The experiment of Example I was repeated with the exception that the hydrogenolysis reactor was operated at 65° C. After 4 hours of operation, the alcohol conversion was 99%, and after 24 hours of operation the conversion was 97%.

EXAMPLE III

The experiment of Example I was repeated with the exception that the hydrogenolysis reactor was operated at 45° C. After 4 hours of operation the alcohol conversion was 82%; and after 24 hours of operation, the conversion was 55.5%.

EXAMPLE IV

The spent catalyst from Example III was regenerated by passing cumene over the catalyst at the rate of 3 litres/hour for 30 minutes, at 150° C. The reactor was then operated as in Examples I, II, and III and the initial conversions were again 99%.

EXAMPLE V

The epoxidation procedure carried out in Example I is carried out using ethylbenzene hydroperoxide instead of cumene hydroperoxide. The resultant alphaphenylethanol is subjected to hydrogenolysis at temperatures of 80° C., 65° C., and 45° C. as described in Examples I, II and III. The results obtained are similar to those obtained with the dimethylphenylcarbinol. The deactivated catalyst from the 45° C. run is regenerated as in Example IV using ethylbenzene as the solvent.

EXAMPLE VI

The epoxidation procedure of Example I is carried out using p-ethyltoluene alpha-hydroperoxide instead of cumene hydroperoxide. The resultant alcohol is subjected to hydrogenolysis at temperatures of 80° C., 65° C., and 45° C. as described in Examples I, II and III. The results are similar to those obtained with the dimethylphenylcarbinol. The deactivated catalyst from the 45° C. run is regenerated as in Example IV using p-ethyltoluene as the solvent.

EXAMPLE VII

The epoxidation procedure of Example I is carried out using alphaphenyl betamethylpropyl hydroperoxide instead of cumene hydroperoxide. The resultant alphaphenylbetamethylpropanol is subjected to hydrogenolysis at temperatures of 80° C., 65° C., and 45° C. as described in Examples I, II and III. The results are similar to those obtained with the dimethylphenylcarbinol. The deactivated catalyst from the 45° C. run is regenerated as in Example IV using the corresponding hydrocarbon with the same skeletal structure as solvent.

EXAMPLE VIII

The epoxidation procedure of Example I is carried out using alpha-tetralin hydroperoxide instead of cumene hydroperoxide. The resultant alpha-tetralin alcohol is subjected to hydrogenolysis at temperatures of 80° C., 65° C., and 45° C. as described in Examples I, II, and III. The results are similar to those obtained with the dimethylphenylcarbinol. The deactivated catalyst from the 45° C. run is regenerated as in Example IV using tetralin as the solvent.

EXAMPLE IX

The epoxidation procedure of Example I is carried out using alpha-alphadimethylparaisopropylbenzyl hydroperoxide instead of cumene hydroperoxide. The resultant alpha-alphadimethylparaisopropylphenylcarbinol is subjected to hydrogenolysis at temperatures of 80° C., 65° C., and 45° C., as described in Examples I, II and III. The results are similar to those obtained with the dimethylphenylcarbinol. The deactivated catalyst from the 45° C. run is regenerated as in Example IV using p-diisopropylbenzene as the solvent.

WHAT WE CLAIM IS:—

1. A process for the hydrogenolysis of an alpha-aralkyl alcohol to form the corresponding aralkane which comprises carrying out the hydrogenolysis reaction with the alpha-aralkyl alcohol in the liquid phase in the presence of a platinum group metal catalyst and at a temperature above 50°C but not above 120°C.
2. A process according to claim 1, wherein

the hydrogenolysis is carried out at a temperature of above 80°C.

3. A process according to claim 1 or 2 wherein the catalyst is palladium.

5 4. A process according to claim 1, 2 or 3 wherein the alpha-aralkyl alcohol is alpha phenylethanol and the product is ethylbenzene.

10 5. A process according to claim 1, 2 or 3 wherein the alpha-aralkyl alcohol is dimethylphenylcarbinol, and the product is cumene.

6. A process according to claim 1, 2 or 3 wherein the alpha-aralkyl alcohol is alpha-tetralin alcohol and the product is tetralin.

15 7. A process according to any of the preceding claims wherein the alpha-aralkyl alcohol is the reduction product of an alpha-aralkyl hydroperoxide resulting from the use of the hydroperoxide in epoxidizing an olefinically unsaturated compound.

20 8. A process according to any of the preceding claims wherein the hydrogenolysis is carried out with hydrogen at a pressure of 20 to 1000 p.s.i.g.

25 9. A process according to any of claims 1 to 8 in which the catalyst is a catalyst which has become deactivated through use in the liquid phase hydrogenolysis of an alpha aralkyl alcohol to the corresponding aralkane and

has been reactivated by being subjected to a solvent wash. 30

10. A process of regenerating a catalyst of a platinum group metal which has become deactivated through use in the liquid phase hydrogenolysis of an alpha-aralkyl alcohol to the corresponding aralkane according to any of claims 1 to 8, which process comprises 35

subjecting the catalyst to a solvent wash. 11. A process according to claim 9 or 10, wherein the solvent with which the deactivated catalyst is washed is the alpha-aralkyl alcohol. 40

12. A process according to claim 9 or 10 wherein the solvent with which the deactivated catalyst is washed is the aralkane. 45

13. A process for the hydrogenolysis of an alpha-aralkyl alcohol to form the corresponding aralkane in accordance with claim 1 and substantially as herein described and exemplified. 50

14. An aralkane when produced by the process of any of claims 1 to 9.

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